

RING CLOSURES FOR THE SYNTHESIS
OF α,β' -DIPYRIDYLS

BY
DAVID JEFFERSON WALLACE

B.S., Murray State College, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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RING CLOSURES FOR THE SYNTHESIS OF α,β' -DIPYRIDYLS

Prior to this time, no synthesis of α,β' -dipyridyls has been available in which substituents were present on either ring. Due to the structural similarity of these compounds to nicotine and anabesine, a study of methods for the synthesis of substituted α,β' -dipyridyls was undertaken, in order to make these compounds available for pharmacological and insecticidal study.

Nicotine has been shown to have insecticidal activity and marked pharmacological properties. It shows three phases of action on the body; a primary stimulation, a secondary depression, and a curare-like effect on skeletal muscle. It is hoped that one of these effects, useful if found alone, may be emphasized over the others in the α,β' -dipyridyls.

DISCUSSION OF RESULTS

Three different approaches were made to this problem, each involving synthesis of one of the pyridine rings by ring closure of a linear chain.

The first method involved synthesis and attempted ring closure of 4-(2-cyanoethyl)-amino-3-penten-2-one. Numerous conditions usually effective for aldol reactions proved unsuccessful. Had the ring closure worked, it was intended to substitute a 2-pyridyl group for the cyano group in the starting material. This would give a dihydrodipyridyl on closure, which is easily oxidized to a dipyridyl. An interesting infrared study was made on the β -amino- α,β -unsaturated ketones. These compounds, which are vinylogs of amides, were found, probably by coincidence, to have absorption maxima in the same regions as amides.

The second method involved the synthesis and attempted ring closure of *N*-(2-[2-pyridyl]-ethyl)-*N*-(2-carbethoxyethyl)-methylamine. Catalysts and conditions favorable for

this Claisen type condensation failed to produce the desired reaction. Such a closure would yield 1-methyl-3-(2-pyridyl)-4-piperidone. This could be reduced, dehydrated, then dehydrogenated to the dipyridyl.

The final method was a pyrolysis of a polyenic oxime such as the oxime of 1-nicotinyl-4-phenyl-1,3-butadiene. This oxime was prepared from the ketone obtained by the reaction of 3-acetylpyridine and cinnamaldehyde in the presence of a small amount of 10% aqueous sodium hydroxide. The compound was also prepared in which crotonaldehyde was used in place of cinnamaldehyde. Pyrolysis of these two oximes gave 2-(3-pyridyl)-6-phenylpyridine and 2-(3-pyridyl)-6-methylpyridine, respectively.

VITA

The author was born in Cleburne, Texas, on May 5, 1923. He was graduated from Tilghman High School in Paducah, Kentucky, in June, 1939. He received the Bachelor of Science degree from Murray State College in August, 1942. In September of that year he enlisted in the Army Signal Corps, and was honorably discharged from the service in January, 1946. In February, 1946, he entered the University of Illinois. During the course of his graduate studies he was employed as a part-time teaching assistant, a special research assistant and held a University of Illinois Fellowship.



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